

## Feature article

# Grafting of hyperbranched polymers: From unusual complex polymer topologies to multivalent surface functionalization



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## ABSTRACT

In this feature article, the grafting of hyperbranched polymers to different substrates is reviewed. Both grafting onto macromolecules with different topologies (homogeneous grafting) and the resulting complex polymer architectures containing highly branched segments as well as their applications are discussed. In the second part grafting of hyperbranched polymers on surfaces, i.e., planar surfaces and spherical particles (heterogeneous grafting), with respect to specific applications, such as bio-repellent surfaces or soluble carbon nanotubes is described. In all cases, the one-step synthesis and the resulting highly branched topology of the hyperbranched building blocks is beneficial for the convenient introduction of a large number of functional groups to the substrates. These multifunctional hybrid materials open interesting options for applications, e.g., for highly functional nanoparticles or nanocomposites.

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## 1. Introduction

Hyperbranched polymers (HBPs) have become an established class of macromolecules since the first mentioning of the term “hyperbranched” by Kim and Webster in the late 1980s [1]. Their synthesis is usually achieved by a single reaction step, providing a highly branched polymer topology with a certain similarity to perfectly branched dendrimers, however, avoiding demanding multistep-synthesis and challenging purification procedures at the expense of a random branching pattern [2–4]. Within the last decade, progress in the synthesis of HBPs has paved the way for several highly branched polymer systems with controlled molecular weights, defined degree of branching and low polydispersities [5,6]. Besides the interest in hyperbranched homopolymers, grafted HBPs (=covalently or non-covalently attached to a substrate) have increasingly been used for the generation of hybrid structures, be it in the field of complex polymer topologies or for surface and particle functionalization. In this case, one has to distinguish between homogeneous grafting, if soluble substrates are used and

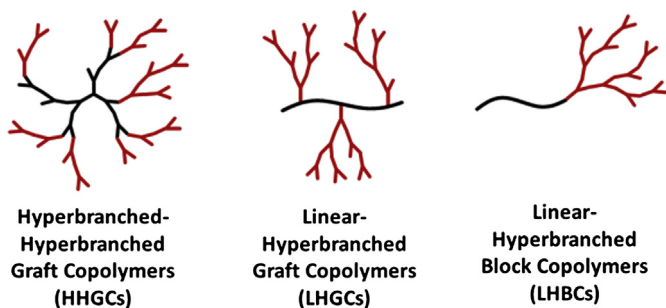
heterogeneous grafting, if non-soluble substrates like metal nanoparticles or silicon wafers as surface substrates are used. HBPs are characterized by a high number of functional groups in combination with a rapid synthesis. The structures allow applications ranging from drug-delivery systems based on polymers with non-linear topologies to antimicrobial surfaces and therapeutic imaging compounds as well as sensors or other biomedical devices [7]. Another key aspect is their utilization as soluble supports in solutions or dispersions, if HBPs are grafted onto spherical particles, nanocrystals, beads or carbon nanotubes [8–10]. Here, the multitude of functional groups of the grafted HBPs promotes solubilization of the substrates in suitable solvents.

In this feature article, recent advances in the field of grafted HBPs are covered. We differentiate between several substrates depending on their macroscopic topology and “dimension” (Fig. 1). In the first part, complex polymer architectures containing grafted HBPs are discussed with respect to theory, synthesis and applications. In most cases, the HBPs are grafted from/to linear chains, which are 1-dimensional (linear) substrates, but also the grafting onto prefabricated hyperbranched polymers (3-dimensional) will be discussed (homogeneous grafting). Second, HBPs grafted on surfaces are reviewed (heterogeneous grafting). Here, one can distinguish between 2-dimensional substrates, such as planar

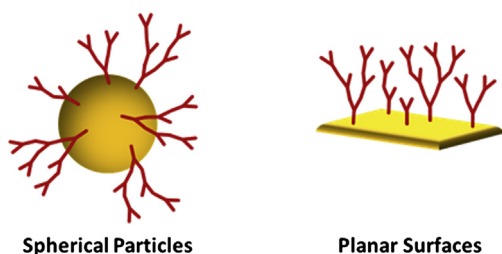
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## a) Complex Polymer Architectures



## b) Surface Functionalization



**Fig. 1.** Overview of various substrates for the grafting of hyperbranched polymer structures: a) complex polymer architectures by grafting from linear and hyperbranched polymer chains and b) functional planar surfaces and spherical particles grafted with hyperbranched polymers.

surfaces and 3-dimensional substrates, mainly spherical particles, which gives rise to multifunctional hybrid structures that are valuable for various applications, such as functionalized nanoparticles and nanocomposites. From a general perspective, the grafting of HBPs is a promising approach to enlarge the fundamental knowledge both in the synthesis and potential future applications of HBPs.

## 2. Complex polymer topologies by grafting onto single polymer chains

Besides composition and functionality, topology is one of the key parameters for synthetic polymers for the next generation of materials [11]. Especially the introduction of branching points that provide additional functional groups and changes in the overall topology lead to a significant variation in materials properties, such as hydrodynamic radius, viscosity or degree of crystallization compared to linear polymers [12]. Additional functional groups permit multiple derivatization reactions compared to linear polymers, where usually only two end groups are accessible. Copolymers containing a linear and a hyperbranched block or two hyperbranched blocks represent an interesting class of hybrid copolymer topologies. The major synthetic challenge in this context is the generation of defined structures with narrow molecular weight distribution, controlled molecular weights and degree of branching (DB) in the hyperbranched block. In this paragraph, we describe recent developments in both theory and synthesis of complex polymer architectures containing hyperbranched building blocks. An overview of the different topologies has been given in Fig. 1 and will be discussed in the following paragraphs in detail. Moreover, other properties, such as self-assembly, crystallization and potential applications are discussed.

### 2.1. Theoretical considerations for the hypergrafting concept

An important technique for the introduction of hyperbranched blocks into various copolymer topologies is the so-called hypergrafting (*grafting from*) strategy, which was first introduced by our group in 2001 [13]. In this case multifunctional (polydisperse) macroinitiator cores  $B_f$  are used for the polymerization of  $AB_m$  monomers. The hypergrafting methodology opens options towards non-conventional topologies (Fig. 1), such as hyperbranched–hyperbranched copolymers (using hyperbranched macroinitiators), linear-hyperbranched graft-copolymers (using multifunctional linear macroinitiators) or linear-hyperbranched block copolymers (using multifunctional block copolymer macroinitiators). Independent of the macroinitiator topology, the hypergrafting strategy can be applied universally. Multiarm star-polymers with a hyperbranched core and linear arms are another major class of complex polymer topologies with HBP building blocks. They have been covered in several reviews and will not be discussed here. [14,15].

A narrow molecular weight distribution is an essential structural parameter for defined complex polymer topologies. Efficient hypergrafting resulting in low polydispersity (PD) of the final polymer can be realized by the slow monomer-addition (SMA) strategy [16]. After initial theoretical works on the synthesis of hyperbranched polymers [17,18], Müller and coworkers derived an expression showing that the number of initiating groups  $f$  of multifunctional macroinitiators is a key parameter to obtain low polydispersities for the SMA of  $AB_2$  monomers (Equation (1)). [19]

$$PD = 1 + \frac{1}{f} \quad (1)$$

thus, for increasing core functionality  $f$ , the polydispersity of the resulting hyperbranched polymer is reduced. In an independent work based on simulation studies, Hanselmann et al. proposed a more general expression to describe the polydispersity for the SMA of  $AB_m$  monomers, confirming Equation (1) (Equation (2)) [20].

$$PD = 1 + \frac{m-1}{f} \quad (2)$$

However, only monodisperse cores in the range of  $f = 2-12$  were taken into account in this study, which are rather interesting for the synthesis of hyperbranched homopolymers. In a recent work by our group, a universal expression for PD valid for the hypergrafting of arbitrary  $AB_m$  monomers from polydisperse macroinitiators  $B_f$  with a number average of functional groups  $\bar{f}$  (Equation (3)) and a polydispersity of  $PD_f$  [21].

$$PD = PD_f + \frac{m-1}{\bar{f}} \quad (3)$$

This result simplifies to Equation (2) for the case of  $PD_f = 1$  and  $\bar{f} = f$ , if monodisperse initiators are used. This shows that not only a high number of initiating moieties  $\bar{f}$ , but also a low  $PD_f$  value is crucial to obtain defined polymer architectures grafted with HBPs.

### 2.2. Hyperbranched–hyperbranched graft-copolymers

When hyperbranched polymers are grafted onto a hyperbranched polymer core, hyperbranched–hyperbranched graft-copolymers (HHGCs) are obtained (Fig. 1a). These materials can be viewed as core–shell structures, which are interesting for a variety of transport applications if polymers with different polarity are used, comparable to multiarm star-polymers with a hyperbranched core and linear chains as a shell [5,15]. Interestingly, only

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